ROMAN AND LATE-ROMAN GLASS FROM NORTH-EASTERN ITALY: THE ISOTOPIC PERSPECTIVE TO PROVENANCE ITS RAW MATERIALS

Filomena Gallo[1], Alberta Silvestri[2], Patrick Degryse[3], Monica Ganio[3*], Antonio Longinelli[4**], Gianmario Molin[1]

[1] Dipartimento di Beni Culturali, Università degli Studi di Padova, Piazza Capitaniato 7, 35139 Padova, Italy

[2] Dipartimento di Geoscienze, Università degli Studi di Padova, via G. Gradenigo 6, 35131 Padova, Italy

[3] Department of Earth and Environmental Sciences - Division of Geology, Katholieke Universitaet Leuven, Celestijnenlaan 200 E, 3001 Heverlee, Belgium

[4] Dipartimento di Fisica e Scienze della Terra, Università degli studi di Parma, Viale G.P. Usberti n. 157/A, 43124 Parma, Italy

ABSTRACT

In this study, the strontium, neodymium and oxygen isotopic composition of Roman (1st-3rd century AD) and late-Roman glass (4th-6th century AD) from Adria and Aquileia, the two most important archaeological sites of North-Eastern Italy, is discussed.

The majority of glass analysed, independent from age, shows values of strontium isotope ratios close to that of modern ocean water, indicating that the source of lime in the glass was marine shell, and likely coastal sands were used in its production. The Nd signature of all Late Roman glasses from Aquileia and of the majority of the Roman ones from Adria, independent from their chemical composition, is homogeneous and higher than -6 εNd, supporting the hypothesis of an eastern Mediterranean origin, probably located on Syro-Palestinian coast. However, the composition of Late Roman samples with HIMT signature, with lower $^{87}Sr/^{86}Sr$ values correlated to higher contents in Fe_2O_3, TiO_2, MgO and lower contents in CaO , suggest an area of origin for this glass on the Egyptian coast. In addition, the different Nd signatures of two Adria Roman glasses (εNd < -7) suggests their primary production in western Mediterranean. Oxygen isotopes proved to be a further diagnostic method to discriminate natron and soda plant ash glass, and different silica sources, in the case of the soda plant ash glass. The combination of isotopic and chemical data supports the hypothesis of an eastern Mediterranean origin for Late Roman glass, which may be produced in few primary workshops on the Syro-Palestinian and Egyptian coast, although not necessarily in the same *ateliers* as have been identified so far. the glass was then imported in the northern Adriatic area. In the case

* Present address: Northwestern University/Art Institute of Chicago - Center for Scientific Studies in the Arts, 2145 Sheridan Road, Tech K111, Evanston, IL 60208, USA

** Present address: via G. Mazzini 128, 56125 Pisa, Italy

of the Roman glass investigated, although the majority of data suggests an eastern Mediterranean origin, on the basis of Nd isotopes and chemical compositions, the existence of other primary glass producers located in the Western Mediterranean canbe suggested.

Keywords: Glass; Roman; Late-Roman; North-Eastern Italy; Strontium; Neodymium; Oxygen; Isotopes; Provenance; Raw materials.

1. INTRODUCTION

Provenance determination of archaeological and historical artefacts relies on the assumption that there is a scientifically measurable property that will link an artifact to a particular source or production site (Degryse et al., 2009a). In this context, mineralogical, petrographical or elemental chemical analyses are the techniques most often used to try to identify where inorganic artefacts were produced. In ancient glass provenancing, chemical composition may provide indications on the glass raw materials, which may then suggest a specific source of supply, although direct relationships between mineral raw materials and the artefacts made from them can be lost at high temperatures (Degryse et al., 2009a). In many recent studies, new questions about glass provenance have been addressed using radiogenic and stable isotopes (e.g., Degryse et al., 2009b, 2010a, 2010b, 2010c; Henderson et al., 2010; Silvestri et al., 2010; Ganio et al., 2012a, 2012b, 2013; Degryse, 2014), since transformations as melting have little effect on the isotopic ratios in glass. In particular, the heavy isotopes of e.g. strontium and neodymium are, due to their relatively high masses at low internal mass differences (Faure, 1986), not fractionated during technical processes. The isotopic composition of the artefact will hence be identical, within analytical errors, to the raw materials of which it was derived, while the signatures of different raw materials used, and hence the resulting artefacts, may differ (Brill and Wampler, 1965; Gale and Stos-Gale, 1982). Conversely, variations in many stable isotope ratios reflect different geological origins, due to different formation processes. The isotopic composition of a raw material is thus largely dependent on the geological age and origin of that material (Brill et al., 1999).

The application of strontium isotopes to the interpretation of ancient glasses depends primarily upon the assumption that the bulk of the strontium of many glasses is incorporated with the lime-bearing constituents in the glass (Wedepohl and Baumann, 2000). These lime-bearing components are likely to be, on one hand, shell or limestone, and, on the other, plant ash, which is usually lime-rich (e.g., Brill, 1970; Verità, 1985). Where $CaCO_3$ was derived from Holocene beach shell, the $^{87}Sr/^{86}Sr$ ratio should reflect that of modern seawater and be close to 0.7092. If, on the other hand, the strontium

was incorporated in the glass in the form of limestone, then it will have an isotopic signature that reflects that of the environment at the time the limestone was deposited, modified by any diagenetic alteration that might have occurred to the limestone over geological time (Freestone et al., 2003). For a glass made using plant ash, the $^{87}Sr/^{86}Sr$ value will reflect the bioavailable strontium from the soils on which the plants grew (Degryse et al., 2010b). It has been assumed that the contribution of natron to the strontium balance of glass is negligible, and minor contributions may be attributed to feldspars or heavy minerals in the silica raw material (Freestone et al., 2003; Degryse et al., 2006a). However, recent study from Brems et al. (2013a) shows that, in some cases (e.g., for glass produced using sand from the western Mediterranean with high Al_2O_3 and an Al_2O_3/CaO ratio higher than 0.25), the Sr isotopic signature of the lime source may be overshadowed by the influence of the Sr from the silicate fraction in the sand.

The introduction of neodymium isotopes in glass studies is recent. Nd in glass is likely to have originated partly from the clay mineral content and partly, but principally, from the non-quartz mineral content of the silica raw material (Degryse et al., 2006b; Degryse and Schneider, 2008). The effect of recycling on the Nd isotopic composition of a glass batch is not significant, apart from mixing sources, and neither is the effect of colourants and opacifiers (Freestone et al., 2005). This offers a great potential in tracing the origins of primary glass production. In this context, a database of Nd isotopic compositions of possible sand raw materials from the Western Mediterranean was recently published (Brems et al., 2013b; Degryse, 2014) and this, together with previous data on the Nd pattern of the eastern Mediterranean sediments (e.g., Freydier et al., 2001; Tachikawa et al., 2004; Brems et al., 2012a), constitutes a useful means of comparison for the growing number of isotopic data on ancient glass. Nd isotopic signatures of the beach sands show, in fact, a decrease in εNd from east to west of Mediterranean basin, ranging from -12.4 for Spanish sands to -3.3 at the mouth of the river Nile (Weldeab et al., 2002; Brems et al., 2013b). Previous studies, carried out on glass dated from the Roman and early Byzantine period (e.g., Degryse et al., 2006b; Degryse and Schneider, 2008; Degryse and Shortland, 2009; Ganio et al., 2012a, 2012b;, Freestone et al., in press) suggested a primary provenance for most of the glass analysed in the Syro-Palestine area and in Egypt. However, some Roman glass showed "exotic" Nd isotopic compositions, which did correspond well to sediments from the western Mediterranean, proving that during the Roman era primary production may also be located outside the Near East.

Oxygen was the first isotope to be used to investigate the provenance of ancient glass. Its potential was pioneered by Brill and co-workers (Brill, 1970, 1988; Brill et al,.1999), which showed that stable isotopes of oxygen have characteristic ranges for certain glass groups. For a typical soda–lime–silica glass, the bulk of the oxygen is about 45%, and approximately 70% of it enters the glass as a

component of the silica. Even in strongly coloured glasses, the bulk of the oxygen is derived from the major components of the base glass (Leslie et al., 2006). For this reason, the oxygen isotopic composition of ancient glass mainly depends on the silica source, with minor influences of flux and stabilizer (Brill, 1970; Brill et al.,1999). In addition, it was experimentally demonstrated that variations in melting time and temperature had no measurable effects on the final oxygen signature of the glass (Brill et al., 1999). Therefore the isotopes of oxygen could be expected to be useful discriminants of raw material sources. In spite of its apparent promise and the important pioneering works of Brill and co-workers, oxygen isotope analysis has not been widely applied in the investigation of glass. Only recently Henderson et al. (2005), Leslie et al. (2006), Silvestri et al. (2010) and Degryse et al. (2010c) have contributed to amplify the database of oxygen isotope data for various archaeological glass samples and possible raw materials.

In this study, isotopic compositions of strontium, neodymium and oxygen are obtained on Roman and late-Roman glass coming from North-Eastern Italy, which, because of its particular position, had a central role in trade as commercial hubs between the Mediterranean and the Padan and Transalpine area. The combined use of Sr, Nd and O isotopic analyses of glass allows different raw materials (sand and/or flux) used for their primary production to be distinguished and characterised. The isotope ratio data obtained for the glass are compared to the sand database, which includes relevant sands from the Eastern and Western Mediterranean, and with isotopic data on coeval glass, already published in literature. These comparisons allow us to advance further hypotheses on location and supply of raw materials and on trade routes during the Roman and late-Roman period.

2. MATERIALS AND METHODS

In the present work 38 samples were selected for the analysis of Sr and Nd isotopes, and the same with the addition of two plant ash glasses (for a total of 40) for O isotope. They are Roman (1st-3rd century AD) to late Roman in date (4th-6th century AD) and come from the North-Eastern Italy, in particular from Adria and Aquileia, the two most important sites in the period and in the area considered. The selection was carefully conducted, in order to represent the various archeological types, colours and the different compositional groups identified and detailed in Gallo et al. (2013, 2014).

In particular, 22 samples were selected from Adria, all Roman (1st-3rd century AD) in date. 12 samples come from compositional group AD/N1, composed of the transparent Adria samples. They are light blue/green, amber, purple, Mn colourless and form an homogeneous group with chemical composition close to that of the 'typical' Roman glass. 4 samples were taken from group AD/N2, all

Sb-colourless glasses and forming a distinct group, produced with a high purity sand, poorer in calcite and feldspars than that used for the 'typical' Roman production. 3 saùmples belong to group AD/A (sample AD-VE-2 for Sr, Nd and O isotopes, plus samples AD-VE-3 and AD-VE-4 for the only O isotopes), glasses produced with a soda plant ash as network modifier. In the Roman period, soda ash glass was uncommon and generally only used to produce particular colours, such as emerald green and black, as in these Adria samples, and its provenance is still debated. Additionally, three other samples were analysed, blue glasses, produced with geochemically different sands (for more details see Gallo et al., 2013). The occurrence of many compositional groups in the Adria assemblage already suggests that different sources of raw materials may have been exploited during Roman times. From the site named "*Casa delle Bestie ferite*" in Aquileia, 18 samples were selected, all late-Roman (late 3rd-6th century AD) in date: 7 from compositional group named AQ/1, 6 from AQ/2, and 5 from AQ/3. The Aquileia groups show a perfect match with the main compositional groups introduced into the Mediterranean area from the 4th century AD onwards, e.g., HIMT for AQ/1, Levantine 1 for AQ/2 and Série 3.2 for AQ/3 (for more details see Gallo et al., 2014). Previous studies on these reference groups suggested a provenance from the Eastern Mediterranean, probably Egypt for the HIMT glass (Freestone et al., 2005) and the coastal strip of Modern Israel and Lebanon for the Levantine 1 and Série 3.2 glass (Foy et al., 2003), although the exact locations should still be identified.

Prior to all isotope ratio analysis, glass samples were carefully cleaned of any alteration products, in order to avoid contamination of results, and then finely crushed in an agate mortar.

The sample preparation for Sr and Nd analyses was performed in a class-10 clean lab with horizontal laminar flow hoods at Ghent University (Belgium). About 100 mg of the powdered samples were put into the Savillex screw-top beakers and a 3:1 mixture of 22 M HF and 14 M HNO_3 was added, followed by heating at 110°C for 24 h. The sample digests were subsequently evaporated and dissolved in a mixture 3:1 of 12 M HCl and 14 M HNO_3 (*aqua regia*). Again, the samples were heated for 24 h at 110 °C and subsequently evaporated to dryness; 2 ml of 7 M HNO_3 was added to the residue and heated on the hotplate for about 30 minutes. The concentrations of Sr and Nd were doubled-checked using a quadrupole-based Perking-Elmer SCIEX Elan 5000 ICP-MS instrument. An internal standard was used to correct for the signal fluctuation, and the calibration was performed with an external standard containing known amounts of the element analysed. For the isolation of Sr and Nd from the concomitant matrix, the sequential extraction chromatographic method, detailed into Ganio et al. (2012c), was followed.

All Sr and Nd isotope ratios were obtained using a Thermo Scientific Neptune multi collector inductively coupled plasma mass spectroscopy (MC-ICP-MS), equipped with a micro-flow PFA-50

Teflon nebuliser, and running in static multi-collection mode. The operating parameters are given in Table 1.

NIST SRM 987 standard was used as reference material for Sr isotope ratio measurements ($^{86}Sr/^{88}Sr$ = 0.1194) to correct for instrumental mass discrimination based on external standardization. The signal intensity obtained for ^{83}Kr was used to correct the Kr interference at m/z =86. Repeated analyses of NIST SRM 987 $SrCO_3$ yielded average $^{87}Sr/^{86}Sr$ ratios with corresponding 2σ uncertainty interval of 0.710263±0.00001, in perfect agreement with the accepted $^{87}Sr/^{86}Sr$ ratio of 0.710248 for this material (Thirlwall, 1991).

For the measurements of $^{143}Nd/^{144}Nd$ ratios, JNdi-1 standard (Geological Survey of Japan) was used as reference material ($^{143}Nd/^{144}Nd$ = 0.51515, $^{146}Nd/^{144}Nd$ = 0.7219). The intensity obtained for ^{147}Sm was used to correct the interference of this element on the Nd signal obtained at m/z = 144. On average, isotope ratios for $^{143}Nd/^{144}Nd$ were measured with an internal precision (2σ) of 0.000008. The ratio is also expressed using the epsilon notation εNd:

$$\varepsilon Nd = \left(\frac{(^{143}Nd/^{144}Nd)_{sample}}{(^{143}Nd/^{144}Nd)_{CHUR}} - 1 \right) \times 10^4$$

where CHUR is a chondritic uniform reservoir, which represents a bulk earth Nd isotope composition deduced from measurements in chondrites: $^{143}Nd/^{144}Nd_{CHUR}$= 0.512638, according to De Paolo and Wasserburg (1976).

Oxygen isotope measurements were performed according to the well-established technique of high-temperature fluorination. About 6–7 mg of the powdered samples were put into the nickel vessels of a fluorination line. After degassing the vessels to less than 10^{-3} mmHg for at least 2 h and freezing them to the temperature of liquid nitrogen, a five-fold stoichiometric amount of BrF_5 was introduced into each vessel and the samples were reacted at 600±5 °C for periods of 20h. The O_2 liberated by the reaction was converted to CO_2 by cycling over hot graphite in the presence of a platinum catalyst and the CO_2 was measured in a Finnigan Delta S mass spectrometer versus a laboratory standard CO_2 prepared from very pure Carrara marble, the isotopic compositions of which, calibrated periodically versus NBS-19 and NBS-20[1], are +2.45‰ ($\delta^{13}C$ versus VPDB) and -2.45‰ ($\delta\ ^{18}O$ versus VPDB). For these calibrations, NBS-19 isotopic values were taken as +1.95‰ ($\delta^{13}C$) and -2.20‰ ($\delta\ ^{18}O$) and

[1] NBS 20 standard material has not been available anymore since a long time. In the laboratory where the analyses were performed, there are reasonable amounts of NBS 19 and NBS 20 re maining from various research centers where Prof. A. Longinelliworked in the recent past. However, NBS 20 is now consumed, raising the serious problem of finding a reliable reference material to calibrate the laboratory standard. The existing LSVEC is isotopically too far from the Carrara laboratory standard, both oxygen and carbon, and is consequently unreliable for calibration purposes.

NBS-20 values as -1.06‰ ($\delta^{13}C$) and -4.14‰ ($\delta\ ^{18}O$). The reported $\delta^{18}O$ values of glass samples are the mean of two consistent measurements of each sample; the standard deviation ranges between 0 and 0.2. Isotopic results are reported in the usual delta terminology versus the VSMOW isotopic standard, delta being defined as follows:

$$\delta\ ^{18}O = [(R_{sample} - R_{standard})/R_{standard}] \times 1000$$

where R is the ratio between the heavy and the light isotope ($^{18}O/^{16}O$).

3. RESULTS AND DISCUSSION

3.1 Strontium Isotopes

Strontium isotope compositions and elemental concentrations of the glass analysed are given in Table 2.

The $^{87}Sr/^{86}Sr$ ratios of the majority of the glass samples range between 0.70884 and 0.70916 (Table 2, Fig. 1), independent from age, site, colour and compositional group, and are close to the ratio of present-day seawater (0.7092). Along with their high Sr contents (Sr= 322-534 ppm, Table 2), this suggests that the source of strontium was marine shell and consequently that beach sands were most likely used. The $^{87}Sr/^{86}Sr$ ratio of the soda ash glass (sample AD-VE-2) is also remarkably similar to the present-day seawater composition ($^{87}Sr/^{86}Sr$ = 0.70894, Table 2). It was demonstrated before that the strontium intake of plants may be dominated by the total (rain)water ingested, and only moderately influenced by the bedrock geology, possibly resulting in a marine signature of the plant ash (Degryse et al., 2010b).

Some samples show clearly different Sr isotopic signatures. The blue sample from Adria AD-B-4, classified as Outlier 3 in Gallo et al. (2013), has a particularly high $^{87}Sr/^{86}Sr$ ratio ($^{87}Sr/^{86}Sr$= 0.71089, Table 2, Fig. 1a). This suggests that it was manufactured with a sand rich in minerals with more radiogenic strontium, probably feldspars, as suggested also by the very high aluminum content observed in its bulk composition (Gallo et al., 2013).

Both purple glasses from Adria show different Sr signatures, lower in sample AD-V-4 ($^{87}Sr/^{86}Sr$ = 0.70854) and higher in AD-V-2 ($^{87}Sr/^{86}Sr$ = 0.70955) (Table 2, Fig. 1b). A similar Sr signature to that of sample AD-V-4 was seen in Mn-containing Roman colourless glass analysed by Ganio et al., (2012b). This variation could be explained by the fact that sand is not the only source of strontium in glass, but also Mn-bearing raw material, added as colourant/decolourant, introduces strontium in the batch (Ganio et al., 2012b; Gallo et al., 2013), and consequently modifies the $^{87}Sr/^{86}Sr$ ratio. The

higher Sr contents (Sr= 592-657 ppm) in the two Adria purple glasses with respect to the other samples (Sr= 322-534 ppm, Table 2, Fig. 1b), together with high Sr contents in other Mn-rich Roman glass (Ganio et al., 2012b), support this hypothesis. The generally low $^{87}Sr/^{86}Sr$ ratios of Mn-containing glass suggest that the Mn source is characterised by a very low Sr isotope ratio. However, the 'inhomogeneous' Sr signature in the two purple Adria samples seems to be indicative of the use of more than one type of Mn-bearing raw material, as already hypothesized in Gallo et al., 2013 on the basis of chemical composition.

Finally, one blue glass from Adria (sample AD-B-7, classified as Outlier 2 in Gallo et al., 2013) and all the samples with an HIMT composition from Aquileia (Group AQ/1 in Gallo et al., 2014) form a distinct group with lower $^{87}Sr/^{86}Sr$ ratios ($^{87}Sr/^{86}Sr$= 0.70832-0.70881, Table 2, Fig. 1b), suggesting the influence of a less radiogenic source of strontium. For HIMT glass, this feature has already been observed in glass from Carthage, North Sinai, Billingsgate and Sagalassos (Freestone et al., 2005, 2009, in press; Degryse et al., 2009b). Furthermore, $^{87}Sr/^{86}Sr$ ratios in HIMT glasses are negatively correlated with oxides such as Fe_2O_3, MgO and TiO_2 and positively correlated with CaO (Fig. 2). The glass with Levantine 1 composition (Group AQ/2 in Gallo et al., 2014) lies at the low iron, titanium, magnesium and high calcium end of the same trend (Fig. 2), suggesting that the HIMT glasses with low Fe_2O_3 are similar in general terms to glasses with Levantine 1 composition and were made using a sand rich in beach shell. As observed by Freestone et al. (2005, in press), these strong correlations indicate that HIMT glass is a mixture of two components: (1) a component rich in Fe_2O_3, MgO and TiO_2 with lower CaO and lower $^{87}Sr/^{86}Sr$, and (2) a component with higher CaO and $^{87}Sr/^{86}Sr$, but lower Fe_2O_3, MgO and TiO_2. The strontium isotopes of component (1) indicate that beach shell was a less significant source of strontium in HIMT glasses with higher iron, magnesium and titanium, as these have lower $^{87}Sr/^{86}Sr$ ratios. The sand therefore contained a significant proportion of its strontium in some other mineral or minerals, such as mafic minerals (e.g., plagioclase, pyroxenes or amphiboles, $^{87}Sr/^{86}Sr$ ratios in general decrease with increasing Fe and Mg). The presence of strontium derived from ancient limestone can be excluded, since the Sr contents are too high to be derived from calcite (Freestone et al., 2003). Strontium measurements on HIMT glasses from North Sinai, Carthage and Billingsgate (London) were reported by Freestone et al. (in press). They noted that the lower $^{87}Sr/^{86}Sr$ ratios of the HIMT range favoured an area of origin on the Egyptian coast, between Alexandria and Gaza, where the Nile strontium isotope signature dominates the sediments (Weldeab et al., 2002). Indeed $^{87}Sr/^{86}Sr$ values in silicates around the Mediterranean are higher than seawater except where the content of material derived from the Nile is exceptionally high, close to the delta in the Southeast (Krom et al., 1999; Weldeab et al., 2002). This model is also consistent with the higher levels of Mg, Fe, and Ti observed in HIMT glasses, since the sands close the mouth of the Nile are richer of heavy

minerals, mainly pyroxenes and amphiboles (Emery and Neev, 1960), which gradually decrease progressing up the eastern Mediterranean coast (Pomerancblum, 1966; Mange and Wright, 2007). However, it should be stressed that HIMT glass from Aquileia, as well as blue glass from Adria (AD-B-7) have $^{87}Sr/^{86}Sr$ ratios ($^{87}Sr/^{86}Sr$= 0.70832-0.70881) comparable to purple glass AD-V-4 from Adria ($^{87}Sr/^{86}Sr$ = 0.70854) (Table 2). These samples are all characterised by high MnO contents (MnO = 1.62±0.62 wt%, in accordance with data reported in Gallo et al., 2013, 2014), negatively correlated with $^{87}Sr/^{86}Sr$ ratios (Figure 2e). This further sustains the hypothesis that Mn sources are characterised by low Sr isotope ratio, which influences the resulting $^{87}Sr/^{86}Sr$ ratios of glass. So far, few studies have been done on Mn sources, and even less is known on the Sr isotopic characteristic of these colourant/decolourant sources; further research is needed to evaluate this hypothesis.

3.2 Neodymium Isotopes

Neodymium isotope compositions and elemental concentrations of the analysed glass samples are given in Table 2.

The glass shows a wide range of Nd isotopic signatures (Table 2). The earlier glass from Adria, dated 1st-3rd century AD, is more heterogeneous, with $^{143}Nd/^{144}Nd$ between 0.51212 and 0.51251, corresponding to values between -2.59 and -10.04 εNd (Table 2). The Late Roman glass from Aquileia, dated late 3rd-6th century AD, shows a much smaller range, with $^{143}Nd/^{144}Nd$ between 0.51236 and 0.51245, corresponding to values between -3.67 and -5.35 εNd (Table 2).

The majority of Roman glass (1st-3rd century AD) from Adria shows εNd values between -4.06 and -5.97, although higher and lower values are also measured (Table 2, Fig. 3a). The large spread in this isotopic composition may indicate the use of multiple sand sources or, alternatively, an intense recycling of glass with different primary origins and thus different signatures. Relationships between isotopic composition and compositional group, colour, type and flux are not observed. An exception is constituted by the small group AD/N2, including three Sb-colourless glasses with very homogeneous Nd composition (εNd= -5.70 to -5.97, Tab. 2, Fig. 3a). This homogeneity was already observed by Ganio et al. (2012a, 2012b) for Sb-colourless glass coming from the shipwrecks Embiez (2nd-3rd century AD) and *Iulia Felix* (3rd century AD), and from Petra in Jordan (sample PE1), Barcino in Spain (sample PD29) and Tienen (sample Tie24) in Belgium, all dated from the 2nd to 4th cents. AD, and characterised by an average εNd value of -5.34±0.20. The general homogeneity of the Nd composition in Sb-colourless glass indicates that they represent a well distinct production and were subjected to a limited or selective recycling.

One sample from Adria (AD-AM-2) has a particularly high εNd (-2.59) (Table 2, Fig. 3a)., which at the moment has similarity only with more or less coeval sample Tie 11 from Tienen (Ganio et al., 2012a).

The Nd isotopic composition of the majority of early Roman Adria glasses is very similar to the signature of the majority of 1st- 4th cents. AD glass published in literature (Degryse et al., 2009b; Ganio et al., 2012a), and also to the known 4th-8th century AD primary production centres in the Levant (εNd= -4.0 to -6.0, Freestone et al., in press; Degryse, 2014), suggesting an analogous provenance, i.e. the eastern Mediterranean, although not necessarily in the same geographical area of aforementioned Late Byzantine glass units, especially for Adria samples with εNd values higher than -4.88. This hypothesis is also reinforced by archaeological evidence, as the discovery of an early Roman glass furnaces in Beirut, Lebanon (Kouwatli et al., 2008).

It should be stressed here that two glasses dating 1st century AD from Adria, one purple with typical Roman composition (sample AD-V-2, belonging to group AD/N1, Gallo et al., 2013) and one blue, the Outlier 1 (sample AD-B-6, Gallo et al., 2013), show relatively low εNd values (εNd= -10.04 and -7.41 in AD-V-2 and AD-B-6, respectively - Fig. 3a). These signatures are inconsistent with any published data from sediments or raw glass in the eastern Mediterranean but correspond well to the range in isotopic values of beach and deep-sea sediments from the western Mediterranean, from the Italian peninsula to the French and Spanish coasts, and from north-western Europe (Degryse and Schneider, 2008; Brems et al., 2013b). The raw materials of the above glass samples likely lie in Western Roman Empire, as already suggested for some 1st-3rd cent. glass from Tienen and Barcino (Ganio et al., 2012a) with comparable εNd values (Fig. 3a). In particular, Italian, French or Spanish sand samples, suitable on the basis of Nd signature and major element composition (Brems et al., 2012, 2013b), show, when the trace elements are compared (Brems et al. 2014), quite different patterns with respect to Adria glasses (Figures 4a-b-c), excluding therefore the hypothesis of possible sources. On the contrary, comparing the Nd isotopic and trace element patterns of the two Adria glasses with those of the MN1 glass (i.e., that obtained using pretreated sand from the Campanian littoral, location mentioned by Pliny the Elder in his Naturalis Historia as suitable source - Silvestri et al., 2006), a general similarity is evident between MN1 glass and sample AD-V-2 (Figure 4d), belonging to group AD/N1 with the typical Roman glass composition. This, in addition to comparable εNd values between AD-V-2 and MN1 glass (Fig. 3a), suggests that the same raw materials may be used, although this actually remains only a speculation due to the low number of compared samples. The lacking of trace element patterns in other Roman glasses with relatively low εNd values, already published in the literature (Ganio et al., 2012a), in fact, limits the possibility of make further inferences on possible sources. In addition, as already observed by Brems et al. (2014), since data are

not yet available for possible sand sources from areas such as Corsica, Sardinia, North Africa and Greece, the existence of competing Roman glass producers with overlapping elemental and isotopic characteristics also in these areas cannot be excluded nor confirmed.

Late Roman glasses (late 3rd-6th century AD) from Aquileia are characterised by more homogeneous εNd values than early Roman glass (Fig. 3b). The separation in three main groups (Group AQ/1, Group AQ/2 and Group AQ/3), recognized on the basis of the chemical composition (Gallo et al., 2014), is well confirmed by the εNd isotopic data. Groups AQ/2 and AQ/3, corresponding to group Levantine 1 and Série 3.2, respectively (Freestone et al., 2000, 2002, 2003; Foy et al., 2003), have εNd values between -3.67 and -4.37, and -4.72 and -5.26 εNd, respectively (Table 2). These values are consistent with Nile dominated sediments and, together with the chemical similarity with glasses produced in the Syro-Palestinian region (Freestone et al., 2000), tend to support the hypothesis of an eastern Mediterranean origin rather than a production with southern Italian sands. However, as shown in Figure 3b, the glasses of Groups AQ/2 and AQ/3 have different Al_2O_3 contents and Nd signatures between them, and different Nd signatures and Al_2O_3 contents (the latter only for AQ3) with respect the Levantine raw glass coming from the primary workshops of Bet Eli'ezer and Apollonia (Israel) (εNd= -4.00 and -6.00, Freestone et al., in press, Degryse 2014), indicating their silica raw materials would not originate from exactly the same locations and suggesting that likely different materials were exploited.

The Nd signature of Group AQ/1 (similar to HIMT glasses) ranges between -3.73 and -5.35 εNd (Table 2). Notwithstanding only some samples show a Nd composition similar to that of other HIMT glasses reported in literature (Fig. 3b, Freestone et al., in press), the εNd values consistent with Nile-dominated sediments, the differences in elemental composition (higher levels of Mg, Fe, Mn and Ti) and the lower $^{87}Sr/^{86}Sr$ ratios observed in these glasses concur to support, for the reasons already discussed in the previous section, the hypothesis of an Egyptian origin.

3.3 Oxygen Isotopes

The results of the oxygen isotopic analysis are reported in Table 3.

The majority of the Roman natron glasses from Adria shows fairly homogeneous $\delta^{18}O$ values, ranging between 15.1‰ to 16.2‰ (VSMOW), with a mean value of 15.6‰±0.2 (Table 3, Fig. 5a). The compositional group, the type and the colour generally do not affect the $\delta^{18}O$ of these glasses, which show, within the range of reproducibility, the same isotopic composition. Only one Sb-colourless glass (AD-I-2) has $\delta^{18}O$ value significantly higher with respect the other Roman Adria natron glasses (17.5‰, Table 3, Fig. 5a). A generally close similarity between the oxygen isotopic compositions of

Adria samples (Groups AD/N1, AD/N2 and Outliers 1, 2, 3) and those of glass coming from the *Iulia Felix* shipwreck (2nd-3rd century AD) is evident, suggesting the use of similar raw materials, although Sb-colourless glasses from *Iulia Felix* show $\delta^{18}O$ values systematically higher than those of coloured or Mn-colourless glasses (Fig. 5a). According to Silvestri et al. (2010), the enrichment in $\delta^{18}O$ does not depend on the addition of decolourisers and is likely due to the greater addition of flux in this glass type, which determines a higher percentage of Na_2O content. The same is not verified for Sb- colourless glass from Adria (group AD/N2), where sample AD-I-2, with the highest $\delta^{18}O$, has the lowest Na_2O value than the other Sb-colourless glasses (17.13 wt% vs 18.56-19.10 wt%, Gallo et al., 2013). Therefore, the most likely explanation is the use of different raw materials (although neodymium data for this sample are lacking). In addition, it is interesting to note that the two Roman samples from Adria with 'exotic' neodymium signature (AD-V-2, AD-B-6, Table 2), indicative of a western Mediterranean provenance of raw materials, are perfectly indistinguishable on the basis of oxygen isotopes data (Table 3, Fig. 5a). A possible explanation of this evidence may come from the similarity in oxygen isotopic composition of probable raw materials (siliceous-calcareous sand), which, in addition to the same flux (natron) in similar ratios, make the glass samples isotopically indistinguishable.

Soda ash Roman glasses (group AD/A) form a homogeneous group, distinct from the natron glass for higher ^{18}O values (16.7‰±0.3 vs 15.6‰±0.2 in natron glass, Table 3, Fig. 5b), suggesting the use of different raw materials. Literature data about similar glass are not reported, since the use of plant ash as a flux in the Roman period is rather rare. For this reason, such Adria samples were compared to some plant ash glasses, dated from the 8th to the 14th century AD, from the eastern Mediterranean (Tyre, Banias and Raqqa; Leslie et al., 2006; Henderson et al., 2005), and from northeastern Italian sites (Grado and Vicenza; Silvestri et al., 2010). The results show that Adria samples do not show any similarity with these glasses (Fig. 5b), having $\delta^{18}O$ systematically higher than Medieval soda ash glass. Taking into account that the addition of ash did not contribute isotopically heavy oxygen and the $\delta^{18}O$ of glass essentially reflects the silica source (Silvestri et al., 2010), the higher $\delta^{18}O$ of the Adria soda ash glass may reflect the use of a different silica source, with respect the Medieval soda ash glass.

The oxygen isotopic data of Late Roman glasses from Aquileia (late 3rd-6th centuries AD, groups AQ/1, AQ/2, AQ/3) are very close to those obtained for the earlier glass from Adria (Group AD/N1), the mean $\delta^{18}O$ values being almost identical (15.6‰±0.2 for Group AD/N1 and 15.5‰±0.4 for Late Roman glasses, Table 3-Fig. 6). The separation in the different compositional groups, recognized by means of elemental chemical analysis (Gallo et al., 2014) and confirmed by Sr-Nd data, is not possible using isotopes of oxygen, since all the results are completely overlapping. In particular, the

correspondence between Groups AQ/2 (Levantine 1 composition) and AQ/3 (Série 3.2 composition) was well expected since, on the basis of Sr-Nd results, it was supposed they were both made with a Levantine sand. On the other hand, the close similarity of $\delta^{18}O$ values for Groups AQ/1 (HIMT composition) and those AQ/2 and AQ/3 is more surprising, as AQ/1 is thought to have been made from Egyptian sands (see previous sections). However, the sands of the Levantine coast are primarily derived from Egypt, being transported to the Mediterranean by the Nile and moved up the eastern Mediterranean coast by marine currents and longshore drift (Emery and Neev, 1960; Pomerancblum, 1966; Stanley et al., 1997). Thus, the silicate components of the sands used for all the natron glasses may have ultimately originated in the same region, and therefore may carry a similar oxygen isotopic signature (Leslie et al., 2006).

Comparisons among samples analysed here and other data already present in the literature show interesting analogies and differences. The $\delta^{18}O$ values of Late Roman/Early Medieval glasses (HIMT and Levantine 1) from Grado, located in the northernmost coast of the Adriatic Sea, show a very good overlap with the present data (Fig. 6), suggesting that the same glass type was used in both the cities. Furthermore, this evidence tends to support the hypothesis of a centralised production, organized in few primary workshops which supplied both Aquileia and Grado. Conversely, the Levantine and HIMT glasses measured by Leslie et al. (2006) appear mostly lower in $\delta^{18}O$ values than the data in the present study (Fig. 6), despite their chemical similarity. As already suggested by Leslie et al. (2006) and Silvestri et al. (2010), a possible explanation for the differences in oxygen composition could be the exploitation of different raw materials on the coast of the eastern Mediterranean, as also already suggested by Nd data. Supporting this possibility are the isotopic compositions of two Belus samples, which have different ^{18}O values, due to different ratios between most abundant minerals (quartz and calcite), even though they were sampled from two different sites 200 m from each other (Silvestri et al., 2010). Moreover, another possibility may be the use of different sources of natron, with distinct isotopic signature which influenced the final glass in a different way (Silvestri et al., 2010).

4. CONCLUSIONS

The combined analyses of strontium, neodymium and oxygen isotopes proved to be a useful supplement to the chemical characterisation for tracing the type and provenance of raw materials in Roman and Late Roman glass.

The majority of natron glass here analysed, independent from age, shows values of strontium isotopes close to the modern ocean seawater ($^{87}Sr/^{86}Sr$=0.7092), indicating that the source of lime was marine shell, and coastal sands were likely employed in its production. Mn-bearing colourants can also introduce strontium in the batch, modifying its total content and isotopic signature, as suggested by the purple glass samples from Adria. $^{87}Sr/^{86}Sr$ values, generally lower the modern ocean seawater, characterise the Late Roman glasses with HIMT composition from Aquileia (Group AQ/1), suggesting the influence of a less radiogenic source of strontium.

On the contrary, the Nd signature of all Late Roman (late 3rd-6th century AD) glasses from Aquileia, independently from the compositional group, is homogeneous and higher than -6 εNd. Comparable values are also shown by glass samples coming from the 4th-8th century AD primary workshops in the Levant. In addition, Groups AQ/2 and AQ/3 (similar to Levantine 1 and Série 3.2 reference groups, respectively) have a chemical composition close to contemporary glass produced in several Levantine workshops. Therefore, the chemical and isotopic data of these glasses support the hypothesis of an eastern Mediterranean origin, likely in the Syro-Palestinian region, although not necessary in the same workshops reported in literature. On the other hand, Group AQ/1 (similar to HIMT glasses), which show similar Nd signatures, are distinguished from Levantine glasses by lower $^{87}Sr/^{86}Sr$ values, also correlated to higher contents of Fe_2O_3, TiO_2, MgO and lower CaO. This indicates that they were produced from geochemically distinctive, but geographically proximal sands. So far, the chemical and isotopic data suggest an area of origin on the Egyptian coast.

The primary origin of 1st-3rd century AD glasses is more difficult to define. The large spread in their Nd isotopic composition suggests the use of multiple sand sources or, alternatively, an intense recycling of glass with different primary origins. Sb-colourless glasses represent an exception, since their homogeneous Nd isotopic composition indicates that they are a well distinct production and were subjected to a limited or selective recycling. As the Late Roman glass from Aquileia, the majority of Roman glass coming from Adria shows a relatively high Nd signature (εNd > -6), similar to that of aforementioned 4th-8th century AD primary production centres located in the Syro-Palestinian coast, pointing to an analogous provenance. However, the slight but clear differences in major element chemistry among Roman Adria glasses and the Byzantine glass produced in the Levantine workshop raise the problem of a possible different origin. Notwithstanding it is probable that these variations could be due to exploitation of different sands along the Syro-Palestinian coast, the use of other primary sources cannot be completely excluded.

It should be stressed that two Roman glasses with a different Nd signature (εNd < -7) have been identified in the Adria sample set. These values are inconsistent with any sediment in the eastern

Mediterranean and tend to locate primary production in western Mediterranean or north-western Europe, as already suggested by other authors for other Roman glass with "exotic" Nd signature.

For what concerns oxygen isotopes, it was observed that the contribution of both flux and sand to the isotopic composition of the glass makes it a somewhat less powerful tool than strontium and neodymium in provenancing raw materials. Overall, oxygen isotopes proved to be a diagnostic method to discriminate natron and soda plant ash glass, and different silica sources, in the case of the soda plant ash glass.

In summary, the combination of isotopic and chemical data support the hypothesis of an eastern Mediterranean origin for the Late Roman glass, which may be produced in few primary workshops, located on Syro-Palestinian and Egyptian coasts, although not necessarily in same *ateliers* so far identified, and then imported in northern Adriatic area. This evidence does not exclude the possibility that secondary workshops could have been active in this area and, in this respect, future studies on production indicators (especially chunks), never analysed from the archaeometric point of view, are desirable.

In the case of Roman glass, although the majority of data so far acquired suggests an eastern Mediterranean origin, on the basis of Nd isotopes and chemical compositions, the existence of other primary glass producers located into Western Mediterranean is also indicated. However, the number of samples with these "exotic" compositions is low, and further isotopic analyses on Roman glass represent interesting subject for future works.

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TABLE HEADINGS

Table 1: MC-ICP-MS operating parameters.

Table 2: Sr-Nd isotopic data and elemental compositions of Roman and late Roman glass from Adria and Aquileia. Compositional groups, as reported in Gallo et al. (2013, 2014), are shown for each sample (nd: not detected).

Table 3: $\delta^{18}O$ (VSMOW) of Roman and Late Roman glass form Adria and Aquileia. Compositional groups, as reported in Gallo et al. (2013, 2014), are shown for each sample.

FIGURE CAPTIONS

Figure 1: Strontium isotope ratio ($^{87}Sr/^{86}Sr$) *vs* strontium content (1000/Sr) for (a) all analysed Roman and late Roman glasses, subdivided by compositional groups as reported into Gallo et al. (2013, 2014); (b) all glasses without Outliers 1, 2, 3. Isotopic signature of Modern Ocean Seawater indicated by dotted line.

Figure 2: $^{87}Sr/^{86}Sr$ ratios *vs* (a) Fe_2O_3 (wt%); (b) TiO_2 (wt%); (c) MgO (wt%), (d) CaO (wt%) and (e) MnO (wt%) contents in Groups AQ/1 (◇) with HIMT composition and AQ/2 (△) with Levantine I composition from Aquileia. R^2 values in all bi-plots and samples AD-B-7 (+) and AD-V-4 (□) from Adria in (e) also shown.

Figure 3: (a) Al_2O_3 (wt%) contents vs εNd of (a) Roman (1st-3rd century AD) samples from Adria; (b) late Roman (late 3rd-6th century AD) samples from Aquileia. Literature data for Roman glass with εNd < -6 (grey symbols, from Ganio et al., 2012a) and data for Apulia (from Brems et al., 2012; 2013b) and MN1 glass samples also reported in (a). Literature data for HIMT and Levantine glasses reported in (b) (grey symbols, from Freestone et al., in press).

Figure 4: Trace element concentrations normalised to the mean abundance in the Earth's continental crust (Wedepohl, 1995). Black continuous lines: Adria samples with εNd < -6 (AD-V-2; AD-B-6). Grey dotted lines: sand samples with εNd < -6 (a) IT01, IT34; (b) SP20 SP22, SP43, SP45, SP46; (c) FR16, FR17 (data from Brems et al., 2014); and (e) MN1 glass (data from Silvestri et al., 2006).

Figure 5: (a) comparison between $\delta^{18}O$ (VSMOW) values of natron Roman glass samples analysed in this study and those from *Iulia Felix* shipwreck (grey symbols, data from Silvestri et al., 2010); (b) comparison between $\delta^{18}O$ (VSMOW) values of soda ash Roman glass samples analysed in this study (group AD/A), natron glass from Adria (AD/N1) and data from literature (grey symbols, data from Silvestri et al., 2010 for Grado and Vicenza; Henderson et al., 2005 for Raqqa; Leslie et al., 2006 for Tyre and Banias).

Figure 6: comparison between $\delta^{18}O$ (VSMOW) values of natron late Roman/early Medieval glass (groups AQ/1, AQ/2, AQ/3), Roman samples (group AD/N1) analysed in this study and data from literature (data from Leslie et al., 2006 for Bet She'an, Bet'Elizer and Carthage; Silvestri et al., 2010 for Grado).